GEOPHYSICAL RESEARCH LETTERS, VOL. 26, NO.2, PAGES 185-188, JANUARY 15, 1999

An 11-year solar cycle in tropospheric ozone from TOMS measurements

S. Chandra[1], J. R. Ziemke[2] and R. W. Stewart[1]

Abstract. Tropospheric column ozone derived from Nimbus 7 total ozone mapping spectrometer (TOMS) footprint measurements from 1979 to 1992 provide the first observational evidence of changes in tropospheric ozone in the marine atmosphere of the tropics which are out of phase with the stratospheric ozone changes on a time scale of a solar cycle. The estimated changes in tropospheric and stratospheric column ozone over a solar cycle are respectively -2.98 ± 1.31 and +8.63 ± 1.99 Dobson units (DU) or -12.6 ± 5.6 and +3.69 ± 0.86 % from solar minimum to solar maximum. These values are statistically significant at the 2σ level. In comparison, linear trends in tropical tropospheric ozone are not statistically significant. These observations are qualitatively consistent with a modulation effect on tropospheric ozone photochemistry by UV-induced changes in stratospheric ozone. However, in the low NO_x regime of the marine atmosphere, the observed changes are significantly larger than estimated from a photochemical model. Explanation for the solar signal may include subtle solar-induced changes in transport in the troposphere involving low boundary-layer ozone and ozone precursors.

Introduction

It is generally recognized that changes in stratospheric O_3 affect solar UV radiation reaching the surface of the Earth and the photochemical and radiative properties of the troposphere [e.g., *Liu and Trainer*, 1988; *Madronich and Granier*, 1992; *Fuglestvedt et al.*, 1994; *Haigh*, 1996; *Hansen et al.*, 1997]. In addition to changing the radiative balance of the atmosphere, a solar-cycle induced change in stratospheric O_3 induces a solar-cycle modulation of ultraviolet-B (UV-B, 290-320 nm) flux reaching the troposphere. A change in UV-B alters the chain of photochemical reactions affecting the rate of production of OH and several other tropospheric gases, which in turn contribute to the production and loss of tropospheric O_3 [e.g., *Fuglestvedt et al.*, 1994, and references therein].

The purpose of this paper is to present the first observational evidence of changes in tropical tropospheric O_3 associated with the stratospheric O_3 changes on a time scale of an 11-year solar cycle. The data used for this study are tropospheric column O_3 (TCO) in the tropics derived from TOMS high-density level 2 footprint measurements. These data are gridded into monthly-averaged 5° × 5° latitude-longitude bins and cover a 14-year period from January 1979 through December 1992. The derivation of TCO is based on the convective cloud differential (CCD) technique [*Ziemke et al.*, 1998] which takes advantage of persistent high-reflecting clouds near the tropopause in the highly convective equatorial Pacific region. Since TOMS measures column O_3 only above cloud tops, high-reflecting (R>0.9) tropopause-level clouds can be used directly to determine stratospheric column O_3. TCO is then calculated by subtracting stratospheric column O_3 from the total column O_3. The latter is derived from nearby total O_3 measurements under the constraint of low-reflecting (R< 0.2) clouds

In practice stratospheric column O_3 is calculated from high-reflecting clouds in the Pacific region where the greatest frequency of tropopause-level clouds are present. Stratospheric column O_3 is calculated for every 5° latitude band and averaged over longitudes from 120°E to 120°W. These values are assumed to be independent of longitude in a given latitude band. This assumption is based on the zonal characteristics of stratospheric column O_3 in the tropics inferred from Upper Atmosphere Research Satellite (UARS) data which suggest a nearly zonally symmetric distribution of stratospheric column O_3 in the tropics [*Ziemke et al.*, 1998].

TOMS Measurements and Analysis

Solar-Cycle Variation In the Tropical Pacific

To delineate the solar signal on a decadal time scale, we first analyze data from the western Pacific where stratospheric column O_3 is derived from high-reflecting convective clouds without assuming zonal symmetry. We will show later in the paper that the conclusions about the solar-cycle response of the troposphere are essentially the same for the other regions of the tropics, particularly in the marine environment. Figure 1 shows monthly mean time series of stratospheric and tropospheric column O_3 over the tropical western Pacific from January 1979 through December 1992. This period corresponds to the declining phase of solar cycle 21 (1979-1986) and rising phase of solar cycle 22 (1986-1992). To accentuate the solar-cycle signal and minimize the effects of interannual variability, time series in Figure 1 were averaged in the latitude band 15°S-15°N and from longitude 120° E eastward to the dateline. This broad averaging significantly improves statistical confidence in the derived time series by producing a mean number of about 1700 R>0.9 total O_3 measurements per month.

Both stratospheric and tropospheric time series in Figure 1 show strong seasonal cycles modulated by a low-frequency signal of a decadal time scale and are represented by a linear regression trend model (dashed curves shown) with seasonal cycle, linear trend, solar cycle, QBO, and ENSO terms as discussed by *Randel and Cobb* [1994] and *Ziemke et al.* [1997]. The solar-cycle term is represented by the conventional F10.7 cm solar flux time series which varies from about 100 to about 230 units (1 unit = 10^{-22} W m^{-2} Hz^{-1}) from the solar minimum to the solar maximum.

Visual comparison of the time series in Figure 1 suggests a solar-cycle variation in O_3 that is inphase with F10.7 in the stratosphere and out of phase in the troposphere. Solar regression coefficients for tropospheric column O_3 as a function of month are shown in Figure 2 with vertical bars indicating statistical significance at the 2σ limit. Figure 2 suggests a weak seasonality in solar-cycle response in the troposphere. A weak seasonality in

[1]Code 916: NASA Goddard Space Flight Center
[2]Software Corporation of America

Paper number 1998GL900272.
0094-8276/99/1998GL900272$05.00

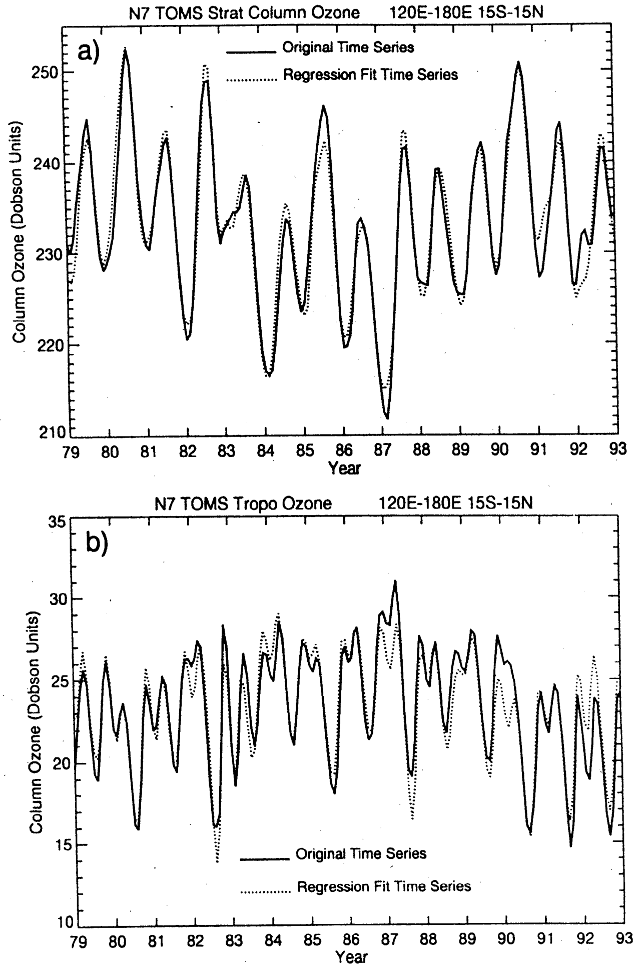

Figure 1. (a) Nimbus-7 TOMS CCD stratospheric column O_3 (Dobson units) for the original time series (solid) and the corresponding regression model fit (dashed). The time series data were derived by averaging all TOMS CCD column O_3 measurements between 15°S to 15°N and from 120°E eastward to the dateline. (b) Same as (a) but for tropospheric O_3.

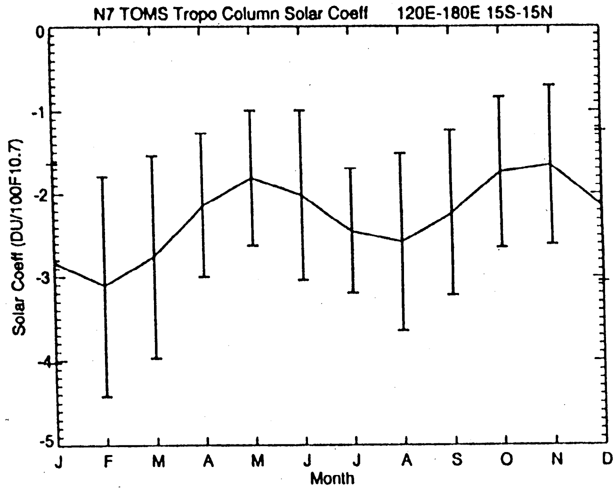

Figure 2. Monthly solar regression coefficients (Dobson units per 100 units of solar F10.7) for the tropospheric column O_3 time series of Figure 1b. Vertical bars represent $\pm 2\sigma$ errors.

solar coefficient is also indicated in stratospheric column O_3 (figure not shown). As shown in Table 1, the mean annual solar responses for tropospheric and stratospheric column O_3 are respectively -2.29± 1.01 DU and +6.64 ±1.53 DU for an increase of 100 units of F10.7 cm flux. A similar analysis for total column O_3 yields a value of +4.35± 0.48 DU/100F10.7 which is the sum of the solar-cycle responses of the stratosphere and troposphere column O_3. In terms of percentage change, the values for the troposphere, stratosphere, and total column O_3 are respectively, -9.69, +2.84 and +1.69% with the 2σ errors shown in table 1. The corresponding values for the solar cycle are respectively −2.98, +8.63 and +5.66 DU or −12.6, +3.69 and +2.20 % assuming a change of +130 units in F10.7 from the solar minimum to the solar maximum.

Table 1. Change relative to +100 unit change in F10.7

Quantity	%/100F10.7(2σ)
Tropo O_3	-9.69 (4.30) [-2.29 (1.01)][a]
Strat O_3	+2.84 (0.66) [+6.64 (1.533)][a]
Total O_3	+1.69 (0.18) [+4.35) (0.48)][a]

[a]Numbers in brackets are in Dobson units.

In estimating solar-cycle components of stratospheric and tropospheric column O_3 it was tacitly assumed that TCO is not affected significantly by changes of the tropopause. Even when clouds overshoot into the stratosphere, the effects on TCO average out in the monthly means since the averaging also includes drops in cloud tops below the tropopause. The seasonal variability in the tropopause height in the tropical Pacific region is about 1 km and the interannual variability is only a few hundred meters [*Gage and Reid*, 1987]. Ozonesonde measurements from several ground-based tropical stations suggest that the major contribution (about 60%) to TCO comes from altitudes below 6 km [*Ziemke and Chandra*, 1998]. A change of 1 km near the tropopause makes only a small change (1-2 DU) in TCO.

Another potential source of error in estimating solar-cycle components may be the long term drift in version 7 TOMS data. *McPeters and Labow* [1996] have shown that the relative drift of TOMS O_3 with respect to an ensemble of 30 Dobson and Brewer stations in the northern hemisphere is negligibly small (0.29% per decade). The relative change of TOMS O_3 with respect to these stations, however, shows a decadal variation of about 1% which appears to be inphase with the solar cycle. The source of this time dependent bias is not known and may be a combination of both TOMS and Dobson errors. The estimate of the solar-cycle response of total column O_3 in Table 1, however, is consistent with the solar-cycle variation of column O_3 inferred from SAGE I /II and SBUV/SBUV2 data [SPARC report, 1998]. UV related changes in column O_3 have also been inferred on the time scale of a 27-day solar rotation [*Chandra*, 1991; *Brasseur*, 1993; *Fleming et al.*, 1995]. Inferred changes are independent of long-term instrumental drift. We note that because of the differencing of total minus stratospheric column O_3 in the CCD method, derived TCO is essentially independent of TOMS instrument calibration errors.

Solar Cycle and Trends in Tropospheric Ozone

The solar-cycle response of tropospheric O_3 inferred from Figure 1, though derived from the O_3 time series in the western Pacific, is a characteristic of most of the marine atmosphere in the tropics. Figure 3 (upper panel) shows the zonal distribution of the solar coefficient, when the O_3 time series in a 5° × 5° latitude-longitude bin are analyzed using the trend model as in Figure 1. Figure 3 shows that the solar coefficients, although smaller than

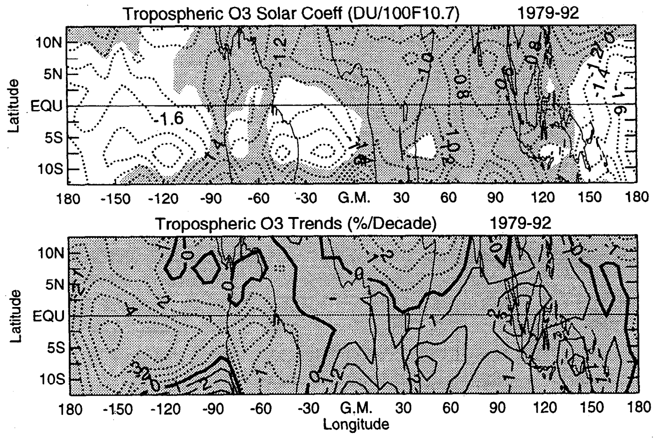

Figure 3. (top) Latitude versus longitude regression model solar-cycle coefficients (units are DU per 100 units of F10.7). Shading indicates regions where the coefficients are not different from zero at the 2σ level. (bottom) Same as (top) but for the linear trend coefficient (units are % per decade). Dark solid curves denote zero trends.

in Figure 2, are uniformly negative throughout the tropics. However, they are statistically significant mostly over the oceanic eastern and western Pacific and the Atlantic regions. The response in these oceanic regions vary from around -1.4 to -2 DU/100 F10.7, or about -2 to -3 DU over a solar cycle.

Figure 3 (lower panel) also shows decadal linear trends derived from the same regression model for the 1979-1992 time period. TCO trends in these analyses are statistically not significant (at the 2σ level) anywhere in the tropical troposphere. It is interesting to note that *Kim and Newchurch* [1998] found a statistically significant positive trend of about +0.6 DU (+10%) per decade in lower tropospheric (below 2.5 km) column O_3 west of New Guinea for the same time period. We note that this represents approximately 20-25% of TCO in the region. They attributed this trend to biomass burning in this region. This trend is comparable to the trend reported by *Jiang and Yung* [1996] and *Kim and Newchurch* [1996] in the latitude range 10-23° S in the eastern Pacific immediately west of South America. The method used in these studies involved differencing of total column O_3 between mountainous and non-mountainous scenes. Our estimated trends in these regions are also positive with values in the range of +0.5 to +0.7 DU (+2 to +3%) per decade, but not statistically significant. The question if these differences can be attributed to differences in the altitude range of the two measurements cannot be answered from this study.

Implications for Tropospheric Ozone Chemistry

In the stratosphere, O_3 is primarily produced through photodissociation of O_2 by solar UV radiation in the Schumann Runge bands (180-200 nm) and Hertzberg continuum and the subsequent recombination of O and O_2 in the presence of a third body. Many of the observed features of stratospheric O_3 related to a solar cycle are qualitatively well represented by photchemical models. However, there are significant quantitative differences between the observed and calculated response of the solar cycle. [e.g., *Brasseur*, 1993; *Fleming et al.*, 1995; SPARC report, 1998].

Tropospheric photochemistry is initiated by the photolysis of O_3 to produce $O(^1D)$. Most of these excited oxygen atoms are quenched and react with ambient O_2 to re-form O_3, but some react with water vapor to produce two OH molecules. The chemistry, subsequent to OH production, depends on the pre-existing chemical background. Our expectations regarding the relationship between tropospheric and stratospheric O_3 burdens is based on the following considerations. The initial reactions leading to O_3 chemical production or loss are:

$$O_3 + h\nu \rightarrow 2OH \qquad (1)$$

$$OH + CO \rightarrow HO_2 + CO_2 \qquad (2)$$

which initially remove an O_3 molecule (the intermediate $O(^1D)$ reactions are not shown). For simplicity we show only CO oxidation. Hydrocarbon oxidation involves the same qualitative arguments. Subsequent reactions may result in either a net loss or a net production of O_3 depending on the fate of the hydroperoxy radical. If the NO_x mixing ratio is low relative to that of O_3, a likely scenario is

$$HO_2 + O_3 \rightarrow OH + 2O_2, \qquad (3)$$

a net O_3 loss. However, at larger NO_x mixing ratios the reaction

$$HO_2 + NO \rightarrow NO_2 + OH \qquad (3a)$$

will dominate leading to a net O_3 production. These issues are treated in greater detail in numerous papers [e.g., *Liu and Trainer*, 1988; *Fugelstvedt et al.*, 1994; *Stewart*, 1995].

To test whether the relationship between stratospheric and tropospheric burdens reported here can result from chemical considerations we have used a box model to perform a series of steady state calculations with varying NO_x and O_3 burden assumptions. The NO_x variations are induced by changing an assumed source of NO over a prescribed range. The box model used has been described by *Stewart* [1993, 1995]. The current version has 64 reactions among 25 variable species. It includes the basic O_x, HO_x, NO_x chemistry along with CH_4, C_2H_4, and C_2H_6 oxidation sequences. Photolysis rates are calculated using the code developed by *Madronich* [1987].

Figure 4 shows the sensitivity in the tropospheric O_3 burden to a change in stratospheric O_3 burden over a range of NO_x values spanning the transition from net O_3 destruction to net O_3 production. For each NO_x value we compute tropospheric O_3 burden for assumed stratospheric burdens of 230 DU and 240 DU. These values approximately correspond to solar minimum and solar maximum conditions as indicated in Figure 1 (panel a). The sensitivity shown on the ordinate in Figure 4 is the ratio $100\times([O_3]_{high}-[O_3]_{low})/[O_3]_{low}$ where the bracketed quantities are tropospheric O_3 burden and the subscripts high and low refer to assumed maximum (240 DU) and minimum (230 DU) stratospheric burden. The transition from correlation to anticorrelation occurs at a background NO_x mixing ratio of around 150 pptv.

The sensitivity of tropospheric O_3 burden to increased photolysis throughout the low NO_x regime is consistent with our qualitative expectations, but is not large enough to quantitatively explain the inferred changes in tropospheric O_3 column. Required NO_x concentrations, in excess of 100 pptv, are probably higher than would be expected in remote marine environments. PEM-West B observations, for example, indicate a mean of 41± 10 pptv [*Thompson, et al.*, 1997].

We have also studied the possible role of water vapor in producing changes in tropospheric O_3 in the marine atmosphere.

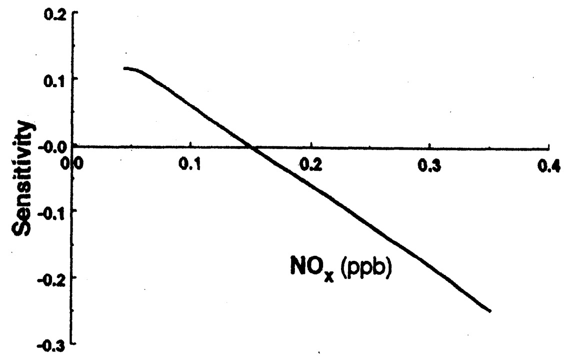

Figure 4. Sensitivity (percentage change) in tropospheric column O_3 as a function of NO_x concentration following a 10 DU increase (230 DU to 240 DU) in stratospheric column O3.

If the NO_x background is low enough for the photochemistry to be a net O_3 sink, increasing water vapor decreases tropospheric O_3. There are probably two factors at work. First, the $O(^1D)$ produced in O_3 photolysis will either react with water vapor or be quenched to the ground state. The latter reaction simply restores O_3 without producing a net loss. As H_2O abundance increases, a greater fraction of $O(^1D)$ produced will react via $O(^1D) + H_2O \rightarrow 2OH$, destroying odd oxygen by increasing its loss. Second, more nitric acid will be produced via $OH + NO_2 \rightarrow HNO_3$. Since this is a sink for odd nitrogen, a vital component in O_3 production, it will further decrease O_3 by reducing its production. Our box model suggests a decrease of about 10-12% in tropospheric O_3 burden as the relative humidity increases from 10 to 95%. Unfortunately, we don't have direct evidence of the solar-cycle variation of water vapor in the troposphere, though such a possibility cannot be ruled out as indicated from recent studies of global cloudiness and the global-mean cloud optical thickness [*Svensmark and Friis-Christensen*, 1997; *Kuang et al.*, 1998]. An explanation for an 11-year solar-cycle signal in TCO may include subtle decadal changes in transport in the troposphere involving low boundary-layer O_3 and O_3 precursors.

Summary

This study provides the first evidence of a decadal solar-cycle signal in tropospheric column O_3 in the marine tropical atmosphere that is out of phase with stratospheric column O_3 but inphase with tropospheric UV. Although the conclusions of this paper are based on tropical O_3 data, the solar-cycle response of tropospheric O_3 should be detectable outside the tropics. Our results indicate solar-cycle variations of tropical stratospheric and tropospheric column O_3 of about 9 and -3 DU or about 4 and -12% respectively. The presence of a solar cycle in tropospheric O_3 appears to reduce the 11-year solar cycle in total column O_3 by about 50%. It is suggested that although the effect of solar-cycle variation of stratospheric column O_3 on solar UV-B radiation entering the troposphere is predictable, the related perturbation imposed on the tropospheric chemical system may give rise to different responses depending on the pre-established background composition. The sensitivity of tropospheric O_3 burden to increased photolysis is consistent with our qualitative expectations, but is not large enough to quantitatively explain the solar-cycle response in the marine atmosphere of the tropics.

A change in TCO on a decadal time scale may have important climatic implications [e.g., *Hansen et. al.*, 1997 and references therein]. Assuming a scaling factor of 0.05-0.08 W m^{-2} DU^{-1} [*Portmann et al.*, 1997], solar-cycle related change in tropospheric column O_3 implies an anomaly of about 0.15-0.25 W m^{-2}. These numbers can be compared to global mean values of ~0.1-0.4 W m^{-2} derived by *Portmann et al.* [1997] that they attributed to tropical biomass burning. The combination of these and other tropospheric radiative forcings could affect both regional and global climate.

Acknowledgments. We thank P. K. Bhartia for helpful discussions and the two anonymous referees for their constructive comments and suggestions.

References

Brasseur, G., The response of the middle atmosphere to long-term and short-term solar variability: A two-dimensional model, *J. Geophys. Res., 98*, 23,079-23,090, 1993.

Chandra, S., The Solar UV related changes in total ozone from a solar rotation to a solar cycle, *Geophys. Res. Lett., 18*, 837-840, 1991.

Fleming, E. L., S. Chandra, C. H. Jackman, D. B. Considine, and A. R. Douglass, The middle atmospheric response to short and long term solar UV variations: Analysis of observations and 2D model results, *J. Atmos. Terr. Phys., 57*, 333-365, 1995.

Fuglestvedt, J. S., J. E. Jonson, and I. S. A. Isaksen, Effects of reductions in stratospheric ozone on tropospheric chemistry through changes in photolysis rates, *Tellus, 46B*, 172-192, 1994.

Gage, K. S., and G. C. Reid, Longitudinal variations in tropical tropopause properties in relation to tropical convection and El Niño-Southern Oscillation events, *J. Geophys. Res., 92*, 14,197-14,203, 1987.

Haigh, J. D., The impact of solar variability on climate, *Science, 272*, 981-984, 1996.

Hansen, J., M. Sato, and R. Ruedy, Radiative forcing and climate response, *J. Geophys. Res., 102*, 6831-6864, 1997.

Jiang, Y., and Y. L. Yung, Concentrations of tropospheric ozone from 1979 to 1992 over tropical Pacific America from TOMS data, *Science, 272*, 714-716, 1996.

Kim, J. H., and M. J. Newchurch, Climatology and trends of tropospheric ozone over the eastern Pacific Ocean: The influence of biomass burning and tropospheric dynamics, *Geophys. Res. Lett., 23*, 3723-3726, 1996.

Kim, J. H., and M. J. Newchurch, Biomass-burning influence on tropospheric ozone over New Guinea and South America, *J. Geophys. Res, 103*, 1455-1461, 1998.

Kuang, Z. M., Y. B. Ziang, and Y. L. Yung, Cloud optical thickness variations during 1983-1991: Solar cycle or ENSO? *Geophys. Res. Lett., 25*, 1415-1417, 1998.

Liu, S. C., and M. Trainer, Responses of the tropospheric ozone and odd hydrogen radicals to column ozone change, *J. Atmos. Chem., 6*, 221-233, 1988.

Madronich, S., Photodissociation in the atmosphere. 1: Actinic flux and the effect of ground reflection and clouds, *J. Geophys. Res., 92*, 9740-9752, 1987.

Madronich S., and C. Grainer, Impact of recent total ozone changes on tropospheric ozone photodissociation, hydroxyl radicals, and methane trends, *Geophys. Res. Lett., 19*, 465-467, 1992.

McPeters, R. D., and G. J. Labow, An assessment of the accuracy of 14.5 years of Nimbus 7 TOMS Version 7 ozone data by comparison with the Dobson network, *Geophys. Res. Lett., 23*, 3695-3698, 1996.

Portmann, R. W., S. Solomon, J. Fishman, J. R. Olson, J. T. Kiehl, and B. Briegleb, Radiative forcing of the Earth's climate system due to tropical tropospheric ozone production, *J. Geophys. Res., 102*, 9409-9417, 1997.

Randel, W. J., and J. B. Cobb, Coherent variations of monthly mean total ozone and lower stratospheric temperature, *J. Geophys. Res., 99*, 5433-5447, 1994.

SPARC/IOC/GAW, "Assessment of trends in the veritcal distribution of ozone", World Meteorological Organization, Report No. 43, 1998.

Stewart, R. W., Multiple steady states in atmospheric chemistry, *J. Geophys. Res., 98*, 20,601-20,611, 1993.

Stewart, R. W.,Dynamics of the low to high NO_x transition in a simplified tropospheric photochemical model, *J. Geophys. Res., 100*, 8929-8943, 1995.

Svensmark, H., and H. Friis-Christensen, Variation of cosmic ray flux and global cloud coverage - A missing link in solar climate relationship, *J. Atmos. Solar-Terr. Physics, 59*, 1225-1232, 1997.

Thompson, A. M., H. B. Singh, R. W. Stewart, T. L. Kucsera, and Y. Kondo, A Monte Carlo study of upper tropospheric reactive nitrogen during the Pacific Exploratory Mission in the western Pacific Ocean (PEM-West B), *J. Geophys. Res., 102*, 28,437-28,446, 1997.

Ziemke, J. R., S. Chandra, R. D. McPeters, and P. A. Newman, Dynamical proxies of column ozone with applications to global trend models, *J. Geophys. Res., 102*, 6117-6129, 1997.

Ziemke, J. R., S. Chandra, and P. K. Bhartia, Two new methods for deriving tropospheric column ozone from TOMS measurements: The assimilated UARS MLS/HALOE and convective-cloud differential techniques, *J. Geophys. Res., 103*, 22,115-22,127, 1998.

Ziemke, J. R., and S. Chandra, On tropospheric ozone and the tropical wave 1 in total ozone, *Proceedings of the XVIII Quadrennial Ozone Symposium*, L' Aquilla, Italy, 12-21 September, 1996, edited by R. D. Bojkov and Guido Visconti, 1, 447-450, 1998.

S. Chandra and R. W. Stewart , Code 916, NASA Goddard Space Flight Center, Greenbelt, MD 20771 (e-mail: chandra@chapman.gsfc.nasa.gov)
J. R. Ziemke, Software Corporation of America, Beltsville, MD 20705

(Received September 25, 1998; revised November 24, 1998; accepted November 25, 1998.)